EXPLOSIVES.

Nobel's Explosives Co., Limited, Glasgow (*Group XXV. No.* 1899).

Nitroglycerine has been successfully applied by Capt. Alfred Nobel to explosive purposes as effected by detonation, and to this end the method of manufacture involves important details. Specimens illustrating (1) dynamite and blasting glycerine, (2) detonators, and (3) electric fuses, are shown, the products of the above well-known firm.

The Schultze Gunpowder Co., Limited (*Group XXV. No.* 1900).

Specimens are shown of the Schultze's patent smokeless gunpowder, made from wood. It is a perfectly white substance, in a granulated form. Wood is rendered explosive by being nitrated, and the product is then granulated. Cartridges charged with it are shown.

ANALYTICAL CHEMISTRY.

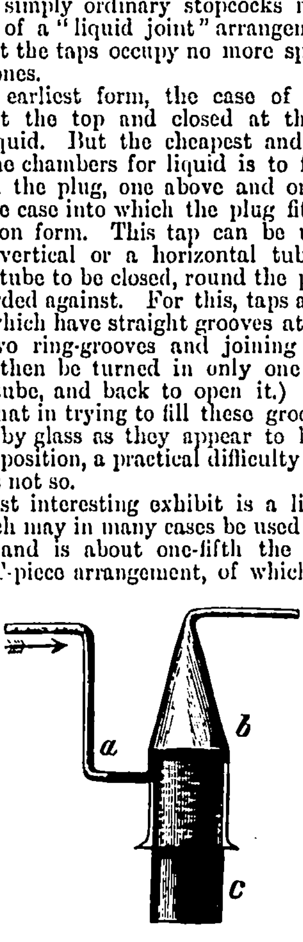
Arnold Eiloart, London (*Group XIV. No.* 1467),

Exhibit specimens of patent airtight stopcocks.

These stopcocks were devised principally to prevent the possibility of leakage occurring in the manipulation of gases in chemical experiments. They are simply ordinary stopcocks made airtight by means of a "liquid joint" arrangement, so contrived that the taps occupy no more space than the ordinary ones.

In the earliest form, the case of the tap was cupped at the top and closed at the bottom to receive liquid. But the cheapest and best way of making the chambers for liquid is to form annular grooves in the plug, one above and one below the bore. The case into which the plug fits is then of the common form. This tap can be used to close either a vertical or a horizontal tube. Leakage along the tube to be closed, round the plug, has still to be guarded against. For this, taps are shown the plugs of which have straight grooves at right angles to the two ring-grooves and joining them. (The plug may then be turned in only one direction to close the tube, and back to open it.) It might be thought that in trying to fill these grooves, entirely closed in by glass as they appear to be, when the plug is in position, a practical difficulty must occur; but this is not so.

The most interesting exhibit is a little arrangement which may in many cases be used instead of a stopcock, and is about one-fifth the cost of one. This is a T-piece arrangement, of which one branch is a tube of half-inch bore into which a smaller tube *a* is fused at right angles; half-an-inch below the joint the wide tube is open; half-an-inch above the joint it begins to taper off (at *b*). An indiarubber plug *c*, not tapering, and covered with a layer of mercury, is pushed upwards past the joint, and so completely shuts off the passage of gas from the side tube, into which also some mercury flows. The passage is opened by slightly lowering the plug. Thus the gas is never in contact with the rubber, but only with glass and mercury.



Addendum to Report of the Exhibit of Messrs. Chapman & Messel. (See p. 520.)

MANUFACTURE OF ANHYDROUS SULPHURIC ACID.

Dr. Messel made his specific gravity determinations at the temperature of 80° F., where all the anhydrides are liquid, though afterwards calculating the results of these to specific gravities at 60° F., when some of the anhydrides become crystallised. It was thought that the readers of this report would be interested in comparing the actual table of results obtained at 80° F., and Dr. Messel has kindly furnished these numbers. The complete table should therefore appear as follows:—

Specimens.	Percentages of SO_3	Specific Gravities.	
		At 80° F. (26·6° C.)	Calculated to 60° F. (15·5° C.)
——	8·3	1·842	1·852
Liquid............	30·0	1·930	1·940
Crystalline mass resembling nitre	40·0	1·956	1·970
	44·5	1·961	1·975
	46·2	1·963	1·977
——	59·4	1·980	1·994
Liquid............	60·8	1·992	2·006
	65·0	1·992	2·006
	69·4	2·002	2·016
Crystallised......	72·8	*1·984*	*1·988*
	80·0	*1·959*	*1·973*
	82·0	*1·953*	*1·967*

Communications.

ON THE ESTIMATION OF SULPHUR IN PYRITES,

BY JOHN CLARK, PH.D.

In the July number of the *Journal of the Society of Chemical Industry* (page 449), Prof. G. Lunge makes some remarks on my process for the estimation of sulphur in pyrites, and states, as his objections, that it estimates the sulphur in galena, and the sulphates of lime and baryta, whilst in the wet process nearly the whole of the useless sulphur is left behind in the insoluble; and I presume that in his opinion this is the cause of the difference between the wet and the dry process. Now, the samples of pyrites upon which I operated contained no weighable quantity of sulphate of barium, less than one per cent. of lead, and from ·1 to ·2 per cent. of lime. In fact, they were typical samples of shipments of Spanish pyrites. I admit that the sulphur in the galena and sulphate of lime is estimated by my process, but it is also estimated by the modification of the wet process employed by the chemists of the Tharsis Company and by Mr. Tatlock, with which alone my process has been compared. The modification to which I have referred consists in treating the pyrites (twenty grains) with aqua regia, and after evaporating to dryness, dissolving in one ounce of hydrochloric acid, filtering, and making up with the washings to a bulk of thirty ounces. After adding the proper quantity of chloride of barium and allowing the precipitate to stand, the clear liquid is decanted and the precipitate washed, first with thirty ounces of hot water containing 300 measured grains of hydrochloric acid, and finally with thirty ounces of pure water. I think it will readily be admitted that with such quantities of acid and water, the whole of the lead and lime usually present in Spanish pyrites will be found in the solution; so that the question at issue between my process and the modification of the wet process is, in my opinion at least, really limited to the solubility of the sulphate of barium in hydrochloric acid, and, whether rightly or wrongly, it is to this cause alone that I attribute the difference in the results. Prof. Lunge may, perhaps, consider that this modification of the wet process is inferior to his own, and quite as objectionable as the dry process, but I would point out, what he has already remarked, that this modification gives very concordant results; whereas, even in the hands of such skilled analysts as the assistants of Fresenius, the wet process, as described by Prof. Lunge, cannot be relied upon to within half a per cent. of sulphur.

◆

THE MANUFACTURE OF PHOSPHORIC ACID FROM PHOSPHORUS.—A BRIEF REVIEW OF THE METHODS IN USE AND A DESCRIPTION OF A NEW PLAN FOR THE PRODUCTION BY THE SLOW OXIDATION OF PHOSPHORUS IN MOIST AIR.

BY ADOLPH SOMMER,

University of California, Berkeley, Cal., U.S.A.

THE author commences by a critical description with details of the various methods of manufacturing phosphoric acid from phosphorus itself, as distinguished from its manufacture from bone earth or glacial phosphoric acid. Eight processes are discussed, viz:

(*a*) oxidation by burning in air;
(*b*) ,, by strong HNO_3 at a low temperature;
(*c*) ,, by dilute HNO_3 at a high temperature;
(*d*) ,, by Br and water;
(*e*) ,, by I and water;
(*f*) ,, by dilute HNO_3 and a little Br;
(*g*) ,, ,, ,, ,, ,, ,, I;
(*h*) ,, ,, ,, ,, ,, ,, I and Br.

The conclusions of the author as to these processes are as follows:—

(*a*) When phosphorus is burnt in air on a manufacturing scale the operation is attended with danger, and the products of combustion are variable. At the same time this is the only possible process if one desire to obtain phosphoric anhydride.

(*b*) When strong HNO_3 is used, as recommended by Von Schroetter, the operation is attended with danger, unless the phosphorus be in the amorphous form, which materially adds to the cost.

(*c*) When excess of dilute HNO_3 at a high temperature is employed, subsequent extraction of the arsenic (a body invariably present) is rendered complex. This method is recommended by the Pharmacopœias.

(*d*) When excess of Br and water is used as recommended by Wagner (*Deut. Ind.* 1875, p. 403), more HBr is formed than H_3PO_4. It is also costly and dangerous. (See this Journal, 1884, p. 20.)

(*e*) The same objections apply to the use of I and water unless iodides are made a collateral object. (See Pettenkofer, in *Dingl. J.* 181, p. 218; and *Ann. der Chem. u. Phys.* 138, p. 51.)

(*f*) When dilute HNO_3, with a little Br as a carrier of oxygen, is employed, action ceases when the HNO_3 becomes very dilute, and heating tends to dissipate Br.

(*g*) The use of I in the place of Br as in (*f*) has the advantage that I is less volatile, but in this case heating tends to convert the P into the amorphous variety.

(*h*) The use of a mixture of Br and I in the place of the single element as in (*f*) and (*g*) with dilute HNO_3 has been attended with fairly good results. (See Markoe in *Am. Jnl. Pharm.* 1875.)

All these methods, except (*a*), have one great objection in common:—viz., that the inevitable excess of oxidising agent, whether HNO_3, Br, or I, has to be removed before the arsenic which is invariably present can be removed by SH_2, or reduced into the metallic state.

The author therefore gives his preference to slow *oxidation at a low temperature by moist air, in which* process there is no excess of oxidising bodies to retard the removal of the arsenic.

Wenzell (*Proc. Am. Pharm. Assoc.* 1882, p. 556) was the first to pratically apply this property of phosphorus. As early as 1796, Pelletier (*Ures Dict. Chem.* 1828, p. 67) had devised a process for the manufacture of "phosphatic acid" by the slow oxidation of cylinders of phosphorus disposed each in a glass tube drawn out at one end to a fine orifice. These glass tubes, to the number of 30 or 40, were placed in a funnel the beak of which was passed into a bottle standing in a plate of water, and the whole was covered with a bell-glass with inlet and outlet for a small current of air. The phosphorus slowly oxidised, and the product deliquesced and dripped into the bottle. This "phosphatic acid" was proved to be a mixture of phosphorous and phosphoric acids by Thenard, Dulong and Leverrier (*Ann. Chem. u. Phys.* 67, 278), but the simultaneous formation of ozone, peroxide of hydrogen, and ammonium nitrate was only recently observed, prominently by Schönbein and Leeds (*Journ. Am. Chem. Soc.* iii. 6). Buchholz (*Beitr. zur Erweit. der Chem.* i. 63) first recommended the production of H_3PO_4 from this body by heating with HNO_3. A. Vogel (*Gmelin*, vol. ii. Lond. 1849, p. 121) and Liebig (*Ib.* p. 128) proposed methods for the elimination of the arsenic, invariably present.

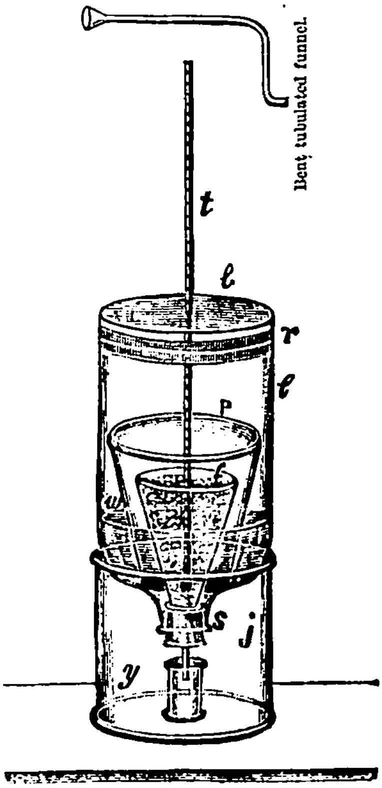
The author first adopted a modified form of the process of Wenzell (*v.s.*). In a shallow trough fitted with a porous cover were placed horizontally cylinders of phosphorus supported on strips of plate glass, and as much distilled water as would suffice to leave about one-eighth of an inch of the phosphorus above water. In three or four days the phosphorus was found to be eaten away down the surface of the water. Portions of the liquid were then successively withdrawn until the whole of the phosphorus was dissolved. In order to reduce the arsenious acid to metallic arsenic, the acid liquid thus formed was heated in a dish to 190° C., at which temperature bubbles of hydrogen phosphide were evolved, marking the completion of the operation. The reaction is expressed by the following equations:—

(*a*) $4H_3PO_3 = 3H_3PO_4 + H_3P$.
(*b*) $3H_3PO_3 + 2H_3AsO_3 = 3OH_2 + 3H_3PO_4 + AsO_2$.

After cooling the liquid was filtered and any further traces of phosphorous acid were oxidised by HNO_3 or Br.

The tediousness of the above induced the author to devise a new process. A glass jar, in which rested a funnel, was placed in a tin can fitted with a cover through which passed a thermometer, the bulb of which descended into the funnel. By an arrangement of holes in the cover a regulated supply of air was admitted, and the inside of the can was lined with cloth, the capillary action of which served to convey sufficient moisture to the air of the can from a measured quantity of water, proportionate to the quantity of phosphorus to be oxidised, placed in the bottom. The cylinders of phosphorus were disposed in the funnel and the bulb of the thermometer buried among them, an atmosphere of CO_2 being used to ensure safety during this part of the operation. According as the temperature ranged above or below 35° C., less or more air was admitted until the temperature remained constant, in which state the oxidation was left to complete itself. When finished, if properly performed, the phosphorus was found to have completely disappeared, and the jar contained a mixture of phosphorous and phosphoric acids which were treated as above described.

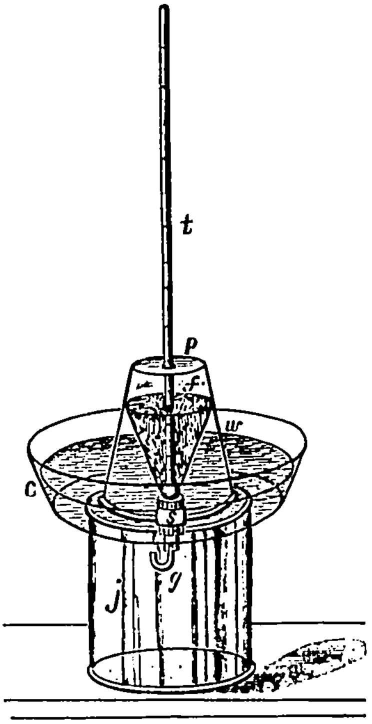
For the construction of a continuous and transparent oxidising chamber, preferably one of white and very clear glass is selected, and the bottom very carefully cut off. This is best done by means of specially-prepared carbon pencils made of powdered charcoal, saltpetre and tragacanth. A common unglazed flower-pot, the largest that will go into the bottle, is inserted into the open bottle so that the bottom of the flower-pot is directly over and in contact with the neck of the bottle. A funnel, the conical part of which is at least an inch shorter than the flower-pot, is then inserted in such a way that the funnel-tube passes through the bottom of the flower-pot and the neck of the bottle. Into the neck of the bottle the funnel-tube is securely fastened by means of a perforated paraffined cork, which must be water-tight.



(*f*) Funnel filled with P.
(*t*) Thermometer.
(*p*) Flower pot.
(*J*) Glass jar.
(*w*) Water.
(*b*) Bottle (inverted).
(*s*) Perforated stopper.
(*y*) Glass cylinder.
(*r*) Strip of paper glued over the cut in the bottle.

This portion of the apparatus is then placed, neck downward, over a large glass jar in which stands a narrow cylinder filled with water. The cylinder is to be in such a position that the end of the funnel-tube will dip into the liquid contained in the cylinder.

Through the centre of the bottom, which was cut off the bottle, a hole of at least $\frac{5}{8}$ of an inch in diameter is drilled. The bottom is then put into its original position on the bottle and fastened by gluing strips of paper over the joint. The hole in the bottom is loosely closed by a cork through which passes a thermometer. When the oxidising chamber is thus completed the cork is removed, and by means of a funnel, having a long bent tube, water poured into the space between the walls of the bottle and the flower-pot, until its level is within a short distance from the upper edge of the funnel within the flower-pot. Then a tube connected with a carbonic acid generator is inserted into the hole and carbonic acid gas passed into the oxidising chamber. When the air within has been entirely displaced by the gas, sticks of phosphorus are dropped through the hole into the funnel until the latter is nearly filled. The thermometer and cork, in the sides of which a few notches have been cut, are then placed into position and the apparatus allowed to stand for about twenty-four hours. If at the end of this time the temperature of the P is below 35° C., a little more ventilation may be given by enlarging the notches in the cork.



(*f*) Funnel filled with P.
(*t*) Thermometer.
(*p*) Flower pot.
(*J*) Glass jar.
(*w*) Water.
(*g*) Bent glass tube.
(*s*) Perforated stopper
(*c*) Tin pan,

The flower-pot in this apparatus performs the same function as is fulfilled in the former by the cloth lining—namely, that of absorbing the water and moistening the air. The acid which is formed runs first into the small cylinder and thence into the glass jar which serves as receiver. Whenever it is seen that that the phosphorus is nearly consumed or the water evaporated, a fresh supply is added through the hole without taking the apparatus apart.

A still simpler form of a continuous oxidising chamber I have constructed in the following manner: Through the bottom of a tin pan a hole of about 1in. in diameter is cut and a tube of tinned iron about ½in. long soldered into it. By means of a perforated cork a funnel is fastened into this hole so that the funnel-tube passes through the bottom, while the body of the funnel is inside of the tin pan. Into the end of the funnel-tube is inserted and fastened by a bit of rubber-tubing, a glass tube bent in a half-circle. A common unglazed flower-pot is inverted over the body of the funnel and a cork with a thermometer inserted into the hole, which is in the bottom of the flower-pot. The whole apparatus is then placed over a glass jar and some water poured into the tin pan. After the pouring of a few drops of water into the funnel, whereby the bend of the glass tube is closed against a downward escape of gas, the filling of the apparatus with carbonic acid and phosphorus is proceeded with in the same manner as has been mentioned under the description of the previous apparatus. When a very large quantity of phosphoric acid has to be made, a number of funnels may be fastened into the bottom of a wooden water tank, and each of them provided, as above described, with a bent glass tube, glass receiver and flower-pot.

The rate at which the phosphorus is oxidised by my method is a comparatively slow one. In an apparatus of style 1, in which the temperature was kept on an average 11° higher than that of the surrounding air, and the phosphorus, which was in the form of a solid cake of nearly 5in. in diameter, exposed a surface of about 18 square inches, the phosphorus was oxidised at the rate of about 10grm. a-day.

The difference between the inner and outer temperature does not seem to be affected to any extent by an increase or decrease of the prevailing temperature, for nearly 200 observations, which were taken at temperatures of the atmosphere ranging from 10° to 22° C., gave, while all other conditions remained equal, an almost constant difference.

The acid which collects in the receivers has a specific gravity of about 1·48, and is composed mainly of phosphorous and phosphoric acids in the proportion of 1 to 4, besides water. The exact composition differs with circumstances, and the determination of these circumstances may be the subject of some future paper.

The further treatment of this acid is in every respect the same as has already been described under Prof. Wenzell's process; but an acid prepared by my method has this great advantage over the one prepared by the former process, that it is already highly concentrated and requires very little evaporation before the arsenious acid is reduced.

THE OXIDATION OF PHOSPHOROUS ACID TO PHOSPHORIC ACID BY MEANS OF BROMINE.—BROMHYDRIC ACID A BY-PRODUCT.

BY ADOLPH SOMMER,

University of California, Berkeley, Cal., U.S.A.

THE product of the slow aerial oxidation of phosphorus contains about one molecule of phosphorous acid to four molecules of phosphoric acid, and besides these some impurities, such as arsenious acid and others, mostly derived from the phosphorus. Of these impurities, the arsenious acid is particularly objectionable, and must be removed before the process of oxidising is entered upon. The removal of the arsenic, as has been described in my article on "The Manufacture of Phosphoric Acid from Phosphorus," is best effected by heating the acid to 190° C., subsequently diluting and filtering, after which the acid is ready to be oxidised.

Heretofore nitric acid has been the only substance employed for this purpose; but since the price of bromine has become so low (about thirty-five shillings per lb., in five-lb. bottles), that its cost is no longer prohibitory to its employment in the industries; and, furthermore, since the value of hydrobromic acid has been recognised both in analytical chemistry as well as in therapeutics, it may prove advantageous to substitute bromine for nitric acid in the oxidation of phosphorous to phosphoric acid.

From the equation—

$$\begin{array}{ccccccccc} H_3PO_3 & + & Br_2 & + & H_2O & = & H_3PO_4 & + & 2HBr \\ 82 & & 159\cdot5 & & 18 & & 98 & & 161\cdot5 \end{array}$$

it will be seen that it requires nearly two parts of bromine to every one part of phosphorous acid. But the total acidity of the mixture of phosphorous and phosphoric acids, when of a sp. gr. of 1·48, is about sixty-six per cent., the composition of which approximates the proportion of one molecule (or twelve per cent.) H_3PO_3 to four molecules (or fifty-four per cent.) H_3PO_4. To convert the twelve per cent. of phosphorous acid into phosphoric acid would require theoretically $2 \times 12 = 24$ per cent. of Br. This result agrees very closely with that obtained in practice, when it was found that with an acid of a sp. gr. of about 1·48 there was needed a little over one-fourth of its weight of Br to complete its oxidation. This operation may be performed after the arsenic has been removed, either in a bottle containing the acid and Br by shaking this mixture from time to time (it must, however, not be shaken too often nor too much at one time, since a considerable amount of heat is liberated by the reaction, which may easily reach the boiling point of Bromine 63° C.), or it may be accomplished more rapidly by pouring the two substances into a retort, and keeping the mixture agitated by slowly passing air through it. In order to prevent any Bromine vapour, which is carried off by the air, from contaminating the atmosphere of the laboratory, I cause the air which escapes from the retort to pass through two bottles containing a solution of caustic potash. When the mixture is no longer decolourised on standing for about twelve hours, but retains a permanent orange colour, which is due to an excess of Br, the oxidation may be considered completed. The excess of Br is best removed by the addition of a small portion of the unoxidised mixture of acids, which has been reserved for this purpose.

There remains then only the separation of the bromhydric acid from the phosphoric acid, which is accomplished by a distillation in a retort from an oil bath. The precautions which have been pointed out in a previous article on the manufacture of bromhydric acid, in regard to its liability to decomposition by organic substances, have to be observed here. The mere insertion of the neck of the retort into a well-cooled receiver is sufficient. Neither luting nor rubber connections are necessary. The first portion which comes over consists principally of water (and Br, if this has not been removed in the manner stated above), and should be withdrawn before the bromhydric acid, which does not evaporate to any great extent until a temperature of about 125° C. has been reached begins to distil. The distillation is continued until a temperature of about 180° C. is reached, when the fire is extinguished and the receiver with bromhydric acid detached. The retort and its contents are allowed to stand till cold, when a quantity of water equal to about one-third of the bulk of the contents is poured into the retort. Heat is then again applied and the distillation continued until the temperature in the retort has reached the same height as before. This second distillation serves to remove a portion of bromhydric acid which cannot be removed in the first distillation.

The phosphoric acid which forms the residue in the retort is a black syrupy liquid, which, however, after dilution with water, digestion with about half per cent of purified animal charcoal, and subsequent filtration through white filtering paper (best the brand known as "Chlorine Paper"), becomes perfectly colourless.

The black colour of the phosphoric acid is due to an organic impurity of the commercial Br, which, it is said, is derived from the luting of the stills, in the composition of which tar is used.

The bromhydric acid, which has distilled over, requires to be redistilled before it can be considered sufficiently pure for pharmaceutical purposes.

If the addition of Br is made to an acid, from which the arsenic has not been removed, the entire amount of arsenic will distil over with the bromhydric acid, while the phosphoric acid will be found free from arsenic.

Obituary.

WALTER WELDON, F.R.S.,

FORMERLY PRESIDENT OF THE SOCIETY OF CHEMICAL INDUSTRY.

Walter Weldon was the eldest son of a manufacturer at Loughborough, and was born on the 31st October, 1832. After having employed himself for some years in his father's works, he came to London, in the year 1854, and applied himself to literary pursuits. Of the labours and struggles of the following six years there is little to record. That they were sufficiently arduous and anxious we may well believe from our knowing little about them. They brought him assuredly neither name nor fame; and a writer who, in six years, shall have acquired in no measureable degree a literary reputation, can scarcely be supposed to have discovered prosperity either. Moreover, before coming to London, he had married a young lady of his own age (he was in his twenty-second year), Miss Anne Cotton, of a Derbyshire family. This imprudence, however, was certainly the wisest thing he had yet done, or was perhaps ever to do. Of the sustainment derived in those early days of discouragement and difficulty from the courage, energy, and devotion of his wife, he ever loved to speak; and it is only due to her memory,—for she too has passed away,—here to record it. During this period, he associated himself with the shareholders in a newspaper, proposed to be issued at this time under the title of *The Dial*, incorporated subsequently with the *Morning Star*, an influential Liberal London newspaper of that day. In furtherance of this project, he travelled through the provinces, making acquaintance with many of the country booksellers, who could not fail to be impressed by his energy, and frank and manly bearing. The connections thus established were soon to prove serviceable. He had, in his early years, experienced the need of some periodical, by which the scientific discoveries and movements of the day should be placed on record as they arose, in a popular form, and at a moderate price; and to the establishment of such a publication he now addressed himself. It was originally designed to be a monthly "Register" of all facts and occurrences relating to the progress of Science. But he perceived, or was advised, that a periodical addressed solely to persons interested in science, to be published at the low price needful to reach those for whose benefit he proposed it, was unlikely, in that day, to obtain adequate public support; and he therefore determined to associate with his records of scientific inventions and discoveries, a "register" also of the progress, from month to month, of Literature and Art. In order to give the country trade a personal interest in his project, he arranged that the publication should be issued by each bookseller in the country subscribing for a sufficient number of copies, *in his own name*. It was to be published monthly, and the price was sixpence. On the 1st August, 1860, appeared, in London, the first number of *Weldon's Register of Facts and Occurrences in Literature, Science, and Art.* Among some of the early papers in it, may be noticed one on Mr. Darwin's then recently publislfed work on the "Origin of Species," written, I believe, by Mr. John Marshall. It was followed by others on "Building Stones, why they Decay;" "Recent Elementary Books on Geology," "Spectrum Analysis," "Philosophy of Earthquakes," "The Coal and Guano Dyes," etc., etc. Among the contributors of the more purely literary and artistic papers were Mr. Sala, Mr. Edmund Yates, Mr. Tegetmeier, Mr. Hollingshead, Mr. W. M. Rossetti, Mr. J. Hain Friswell, Mr. Percy Greg, and others who have since become more or less widely known by their writings.

The *Register* was continued for some three years, but it may be doubted whether, at any time, it secured commercial success. The price at which it was issued involved the necessity for a very large sale, and this probably it never attained. Finally, and fortunately for the world, it had to be abandoned.

Mr. Weldon then directed his attention, by what special inducements, at the moment, we possess no sufficient knowledge, to the subject of industrial chemistry. Brought up in the tenets of the school of Swedenborg, to which he was ever deeply attached, he had made the acquaintance of Mr. C. T. Hook, the well-known paper manufacturer of Snodland, near Rochester, who was also a Swedenborgian, and this may possibly have led him to direct his attention to the particular branch of industrial science to which, by "cheapening every sheet of paper in the world,"—to adopt the words in regard to his work of the eminent French chemist Dumas,—he was to be indebted for his fame as a discoverer and a benefactor of his race.